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Formation and Dissociation of Hydrate Plugs in a Water in Oil Emulsion

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In this paper, we present experimental results of the formation and dissociation of methane hydrate plugs in a semi-batch reactor. The plugs are done from water in heptane emulsion (water content from 30 %). The experimental results shows that the formation rate and dissociation rate are controlled by the heat transfer at the wall of the reactor. An unexpected behaviour is observed as the temperature decreases under the 0°C temperature during dissociation and seems to form ice which slows down the dissociation rate.

1. Introduction

When appearing in an industrial context, gas hydrates are rarely welcome. It is typically the case in offshore oil exploitation, as undersea conditions (a few MPa and 3-4°C in temperature) are sufficient for their formation. Consequences may be the blocking of the oil transmission lines, by plugging valves and other transport facilities.

Many studies have been performed concerning thermodynamics and kinetics of gas hydrates crystallisation and on the possible remedies to prevent pipe plugging.

Up to now, so-called thermodynamic additives (such as methanol or glycols) have been frequently used. However the increasingly drastic field conditions (due to greater drilling depths), combined with more and more constraining environmental policies relative to the rejects, has shifted the research activities in that field towards two new classes of low dosage inhibitors (Bloys et al., 1995 ; Lederhos et al., 1996 ; Urdahl et al., 1995 ; Lund et al., 1996 ; Larsen et al., 1998). The first ones are anti-agglomerants, i.e. surfactant compounds, which emulsify water and allow thin hydrate crystals suspension to be transported. The second ones consist of kinetic inhibitors, which may prevent crystals nucleation or growth during a sufficient delay compared to the residence time in the pipeline.

The present study consists firstly in evaluating the action mechanism of an anti-agglomerant additive called Emulflip E102B and its effects on the texture of the plug. The second step of the study focus on the kinetic of dissociation of the plug which has been previously formed.

2. Apparatus description

The reactor cell is a pyrex cylinder. It is filled with a volume of 800 cm³ to 1200 cm³ of water and oil. The cell is located in a stainless steel autoclave in which the pressure can be raised up to 120 bars. The

autoclave is surrounded by a cooling jacket through which glycol is circulated from a cryostatic temperature controller. Two sapphire windows mounted on both sides of the reactor make possible the observation of crystals during crystallization or dissociation. A four vertical-blade turbine impeller ensures stirring of the suspension. The rotation rate can be varied from 0 to 600 rpm.

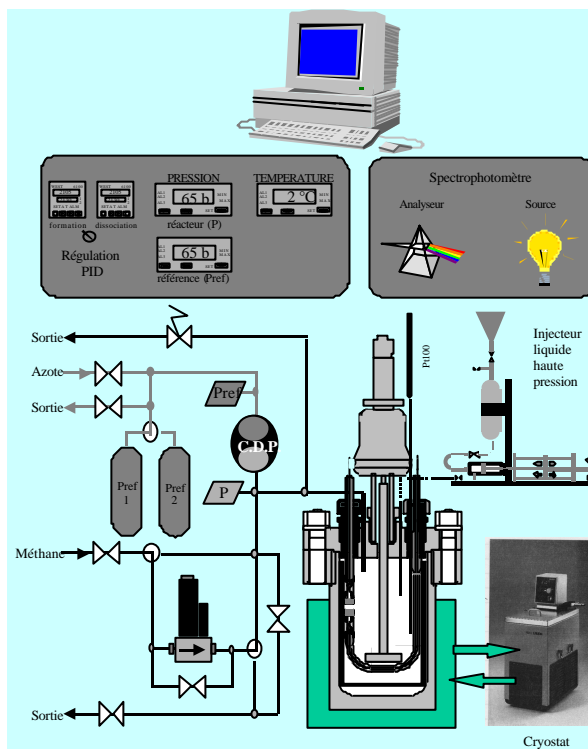


Figure 1
Schematic of the apparatus

Temperature is monitored by a Platinum thermocouple. The turbidimetric sensor is a UV - visible analyser that measures *in situ* attenuation of a polychromatic beam [230 nm, 750 nm] crossing the suspension. Calculating the Particle Density Function (PDF) of a suspension from its turbidity spectrum is theoretically possible (Eliçabe et al, 1989; Crawley et

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al, 1997). This requires several steps that have been discussed in a previous paper by Herri *et al* (1999). The term “particles” refers to the specie which refractive index is different from the bulk, so it could refer to hydrate particles, or water droplets. This technique is fully applicable at low concentration of particle, i.e. the use of turbidimetry is restricted to dilute suspension (about 0.1-1% in particle volume). But, global values such as mean diameter or volume of particles can be retrieve up to 5 % volume.

3. formation experiments

We present here a set of experiment which has been done from a 1200 cm³ of water (30 % vol.) in heptane emulsion with addition of a dispersant (E102) furnished by IFP. The concentration of additive is 0.06 % mass of the total water and oil mass. The starting formation pressure is from 70 bars but is can be increased to 90 bars depending on the ability of hydrates to form quickly.

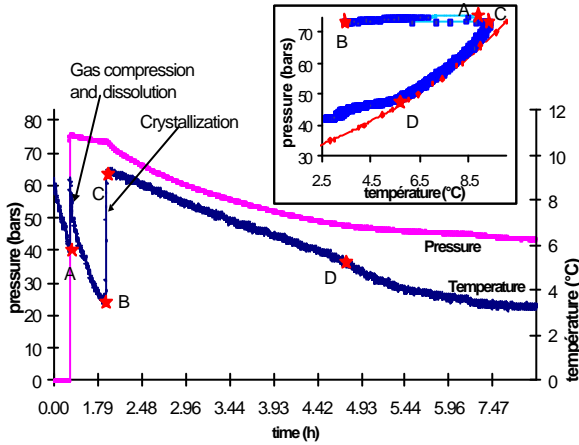


Figure 2

Methane Hydrate formation in a water (30 % Vol.) in oil emulsion in a batch reactor (stirring rate : 400 rpm)

The figure 2 shows a typical experiment of formation. At the beginning, the emulsion is cooled at atmospheric pressure, here down to 6°C. Then the pressure is increased at a maximum value of 75 bars and methane supply is closed and the reactor evolves as a batch system. We observe a first temperature drop due to the gas compression and methane dissolution. Then the temperature continues to decreases down to a sudden new temperature drop due to hydrate crystallisation. The temperature increases to its maximum value, i.e. the equilibrium temperature, which a function of pressure $P : T_{eq}(P)$. Then methane is consumed due by the hydrate crystallisation processes and pressure continues to decrease. In the same manner, the temperature continues to decrease as a $T_{eq}(P)$ function. This is a very interesting point because it allows to identify the limiting step.

The accumulation rate of energy in the system is given by (eq. 1):

$$A_{cc} = \{aV[(1-\epsilon)Cp_{water} + \epsilon Cp_{hyd}] + (1-a)V Cp_{hept}\} \frac{dT}{dt}$$

with

V total volume of the suspension [cm³]

a water volume fraction

Cp volumic heat capacity of water, hydrate and heptane, [J.cm⁻³.K⁻¹]

ϵ water conversion in hydrate $\in [0-1]$

Here the term vCp_{gas} corresponding to the energy accumulation of the gas phase of volume v is negligible.

In a more simple way, we write (eq. 2):

$$A_{cc} = A(e) \frac{dT}{dt}$$

The energy of the reaction is given by (eq. 3) :

$$R_{reaction} = \frac{1}{5.75 \cdot 18} aV \Delta H_R \frac{de}{dt}$$

with

$1 \text{ CH}_4 + 5.75 \text{ H}_2\text{O} \rightarrow \text{hydrate}$

ΔH_R (<0) molar reaction enthalpy [J.(mole CH₄)⁻¹]

18 molar mass of liquid water [18 g.cm⁻³]

The energy rate of methane dissolution is given by (eq. 4):

$$D_{dissolution} = \frac{dC}{dt} (1-a)V \cdot \Delta H_{dissol}$$

ΔH_{dissol} (<0) molar enthalpy of methane dissolution in heptane [J.(mole CH₄)⁻¹.cm⁻³]

Here we assume that the contribution of the dissolution in water is negligible because of the very low methane solubility in water compared to liquid hydrocarbons.

In the presence of hydrate, the concentration C is the liquid hydrocarbon belongs to the range $[H.Peq, H.P]$ where H is the Henry constant. In first approximation, we consider that H is not dependent on temperature and pressure in the temperature and pressure ranges of the experiments which are presented in this paper.

The heat exchange at the wall of the reactor is given by (eq. 5):

$$E_{exchange} = U \cdot A (T - T_{cooling jacket})$$

U exchange coefficient [J.m⁻².K⁻¹]

A reactor exchange surface [m²]

The methane mass balance yields to (eq. 6):

$$\frac{-dn}{dt} = \frac{dC}{dt} (1-a)V + \frac{1}{5.75 \cdot 18} aV \frac{de}{dt}$$

where n is the methane mole number in gas phase of volume v . In fact, because we are in batch reactor, the mole number variation in the gas phase corresponds to the mole flow rate in the emulsion or suspension. In

this equation, the quantity of methane passing in water is assumed to be negligible.

At time t , the general gas law $Pv=z(T,P)nRT$ gives (eq. 7):

$$\left(\frac{1}{P} \frac{1}{z} \frac{dz}{dT} \frac{1}{T} \frac{dT}{dP} \right) \frac{dP}{dt} = \frac{1}{n} \frac{dn}{dt}$$

This equation could be written under the form (eq. 8):

$$\frac{v}{zRT} \left(1 - \frac{P}{z} \frac{dz}{dT} \frac{P}{T} \frac{dT}{dP} \right) \frac{dP}{dT} \frac{dT}{dt} = \frac{dn}{dt}$$

The experimental observation that the Temperature and the Pressure on section CD (figure 2) are equilibrium pressure and equilibrium temperature yields to two major simplifications of the equation. In fact, we can write indifferently that $P=P_{eq}(T)$ or $T=T_{eq}(P)$ where P_{eq} (resp. T_{eq}) is the function giving the equilibrium pressure (resp. temperature) for a temperature T (resp. pressure P).

The first simplification concerns the precedent equation which can be written indifferently (eq. 9,10):

$$v \cdot f(T) \frac{dT}{dt} = \frac{dn}{dt} \quad \text{or} \quad \frac{dP}{dt} = \frac{1}{v} g(T) \frac{dn}{dt}$$

The second simplification concerns the methane concentration in the liquid hydrocarbon (eq. 11).

$$C=H.P$$

Combining the energy balance (eq. 12):

$$A_{cc} = R_{eac} - D_{dissolution} - E_{exchange}$$

And the mole balance (eq. 13):

$$\left(1 + H \frac{g(T)}{v} (1-a)V \right) \frac{dn}{dt} = \frac{-1}{5.75} \frac{aV}{18} \frac{de}{dt}$$

yields to (eq. 14) :

$$\frac{dn}{dt} = \frac{UA(T - T_{cooling\ jacket})}{-\Delta H_R + \frac{A(e)}{vf(T)} - H \frac{g(T)}{v} (1-a)V(\Delta H_R - \Delta H_{dissol})}$$

It appears that, as the temperature and pressure are on the equilibrium curve, the pressure depletion dP/dt and the conversion rate $d\epsilon/dt$ are only dependent of the temperature T and on the ability of the reactor to extract the energy produced by the reaction towards its cooling jacket.

That means that the crystallisation is limited by the energy transfers at the wall of the reactor.

This is an results which differs completely of the case of methane hydrate crystallisation in pure water that we studied previously in Pic *et al* (2001). In fact, crystallisation of methane hydrate in pure water in a batch system is limited by the mass transfer at the upper gas/liquid interface which is very slow and which prevents the suspension from very high temperature drop due to the exothermic character of the hydrate crystallisation.

For methane hydrate crystallisation in water (30 % vol.) in heptane emulsion, the situation is completely different because hydrocarbon can stock a more important quantity of methane which is directly

accessible to the water droplets due to the high liquid/liquid interface. So, as the crystallisation occurs, the crystals can form more quickly by consuming the methane dissolved in the surrounding liquid hydrocarbon. We observe here that the temperature drop is maximum, *i.e.* the temperature rises the equilibrium curve. After that, the crystallisation becomes limited by the heat exchange at the wall of the reactor.

4. Dissociation experiments

Once the hydrates have been crystallized, we perform dissociation experiments. There is two ways to proceed to their dissociation :

- gas depressurisation,
- temperature increase.

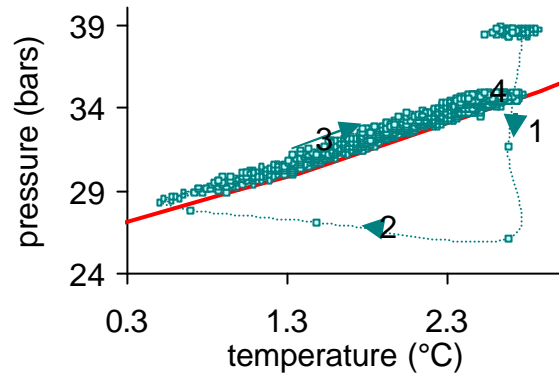


Figure 3

$P(T)$ curve during dissociation of methane hydrate after a sudden depressurisation.

Here are presented results concerning the gas depressurisation. The figure 3 shows a depressurisation from a initial point of (38 bars, 2,7°C). The pressure decrease is done in a few seconds down to 26 bars (step 1). The temperature maintains constant but suddenly decreases as the pressure increases slightly up to the equilibrium condition (~29 bars , ~0,5°) (step 2). Then the (P,T) point evolves slowly along the equilibrium pressure up to (~34 bars, ~2,7 °C) where it stabilises itself. The $P(t)$ and $T(t)$ curves are shown on figure 4 and corresponds to the experiment entitled experiment 2. We can observe the increase of temperature and temperature corresponding to the step 3.

We can give an interpretation of this experimental results under the following description :

- the step one correspond to a sudden pressure depletion which is done by ourselves. Then the exist valve is closed and the reacts as a batch system.
- At the step two, we observe a temperature decrease connected to a pressure increase. This is due to the dissociation of a part of the suspension which release gas and consume energy (dissociation is endothermic).

- The step three corresponds to an evolution along the equilibrium curve of the hydrate toward the equilibrium condition of the reactor, *i.e.* the temperature imposed by the cooling jacket which acts here as a heating jacket because of the initial decrease of the bulk temperature (step 2). This migration along the equilibrium curve is so forced by the heat transfer at the wall and accompanied by an increase of the temperature due to dissociation of a part of the hydrate. The equation eq.14 is already applicable and so the heat transfer is governing the dissociation rate.

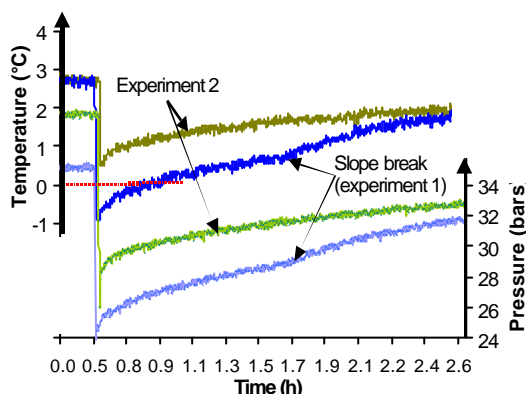


Figure 4

$P(t)$ and $T(t)$ curves during dissociation of methane hydrate after a sudden depressurisation.

The experiment 1 (figure 4) corresponds to another experiment in which the temperature decreases below the 0°C temperature during step 2 (figure 5). Then we observe the ascent of temperature and pressure along the equilibrium curve as the same of the figure 3. The principal difference is observed on figure 4 which shows a slope break corresponding to a increase of ascent rate along the equilibrium curve.

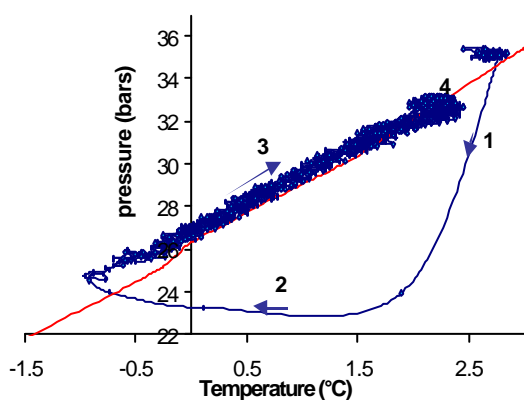


Figure 5

$P(T)$ curve during dissociation of methane hydrate after a sudden depressurisation.

This is an interesting result which can underline the effect of ice formation during hydrate dissociation. In

fact, only a phase transition can explain the slope break. This phase transition could be the disappearance of ice which have been generated as the temperature was below 0°C. If this assumption is valid, this signifies that the ice formation is not a welcome event during dissociation because it slows down the dissociation rate.

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